

# Questioning the existence of a unique ground state structure for Si clusters

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Density functional and quantum Monte Carlo calculations challenge the existence of a unique ground state structure for certain Si clusters. For Si clusters with more than a dozen atoms the lowest ten isomers are close in energy and for some clusters entropic effects can change the energetic ordering of the configurations. Isotope pure configurations with rotational symmetry and symmetric configurations containing one additional isotope are disfavored by these effects. Comparisons with experiment are thus difficult since a mixture of configurations is to be expected at thermal equilibrium.

The determination of the structure of clusters is a difficult task. The standard experimental techniques such as X-ray diffraction and NMR methods that allow to determine the atomic positions in crystals and molecules are not applicable to clusters [1]. The main source of experimental information, ion mobility measurements [2], gives only crude information about the overall shape of a cluster. The exact atomic positions of all the atoms forming the cluster remain unknown. For this reason computational simulations provide a viable alternative to the experimental approach, which has been widely used for silicon clusters. From the theoretical point of view the ground state structure of a solid state system is determined by the global minimum of the Born-Oppenheimer potential energy surface. Finding the global minimum requires global optimization algorithms. Two problems arise in this context. First, most global optimization algorithms give no guarantee for finding the global minimum within a finite amount of computer time. Second, the Born-Oppenheimer energy surface has to be calculated with very high precision.

Concerning the first point there is now a large amount of agreement between different methods for medium size clusters containing up to 19 atoms [3, 4]. Genetic algorithms [5, 6, 7], the big-bang method [8], the basin hopping method [9, 10, 11] and the minima hopping method [12] give typically similar or even identical results. The discrepancies are rather due to different exchange-correlation functionals in different investigations [13].

The existence of a well defined ground state structure is generally taken to be granted for silicon clusters. Silicon clusters are, however, very different from bulk silicon where the second lowest configuration (a fourfold coordinated defect [14]) is 2.4 eV higher than the crystalline ground state. Clusters are frustrated systems, where most of the atoms cannot adopt their favorite fourfold coordination [1]. This can lead to small energy differences between different configurations. The significant deviations of the clusters bond lengths from the crystalline

bond lengths shown in Fig. 1 illustrate this frustration.

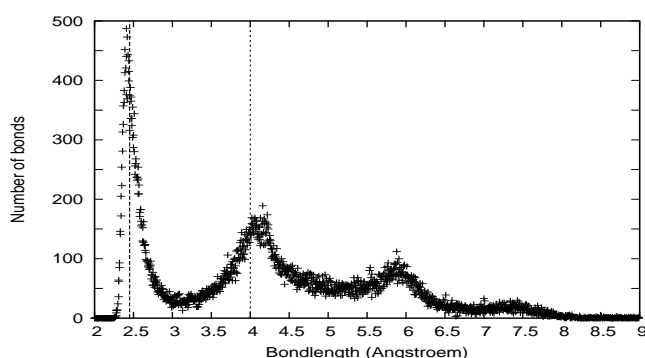


FIG. 1: The bond-length distribution averaged over various low-lying Si17-configurations. The two vertical lines indicate the 1st and the 2nd nearest neighbor distances in the crystal.

In this work we did not only search for the ground state configurations of silicon clusters with up to 19 atoms, but for a large number of low energy configurations. This is possible with the dual minima hopping method (DMHM) [15], which has the property that it explores higher and higher energy configurations after having found the global minimum. Fig. 2 shows the first major result of our investigation, the energies of the 10 lowest configurations of silicon clusters containing 7 to 19 atoms. The energy difference between the global minimum and the second lowest minimum is 0.8 mHa for Si<sub>11</sub>, 0.9 mHa for Si<sub>13</sub>, 2.1 mHa for Si<sub>14</sub>, 3.1 mHa for Si<sub>17</sub> and 3.2 mHa for Si<sub>19</sub>. For Si<sub>13</sub> and Si<sub>17</sub> the 10 lowest configurations are in an interval of roughly 10 mHa. Since room temperature corresponds to  $\sim 1$  mHa, entropic effects play an important role for these clusters.

The results of Fig. 2 were obtained with the PBE [16] functional. Even though this functional is considered to be among the most accurate ones, its accuracy is clearly insufficient to determine unambiguously the energetic ordering of the configurations. For this reason we have performed the most accurate electronic structure calculations that are feasible for these systems, namely quan-

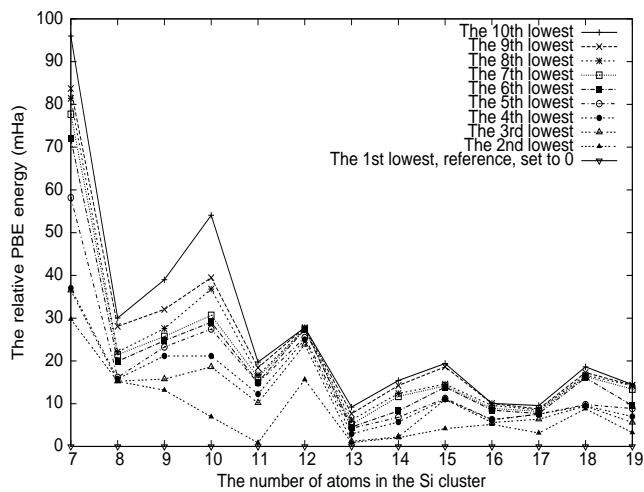


FIG. 2: The dependence of the PBE energy interval for the lowest 10 configurations on the cluster size.

tum Monte Carlo (QMC) simulations. The QMC calculations are performed using the CHAMP code developed by Umrigar and Filippi. The 1s, 2s and 2p electrons of Si are eliminated using a relativistic Hartree-Fock pseudopotential [22]. A Slater-Jastrow type wave function is used as the trial wave function. The orbitals of the Slater determinant are taken from a DFT calculation with the GAMESS [23] code using the B3LYP functional. The parameters of the Jastrow function describing electron-electron, electron-nuclear and electron-electron-nuclear correlations are optimized in variational Monte Carlo using energy minimization [24]. Diffusion Monte Carlo method calculates the final energies, which are presented in Table I. The corresponding configurations are shown in Fig. 3. The QMC energies have error bars of the order of 1 mHa which is just enough to discriminate between the different energies. Even though the Monte Carlo results change the energetic ordering of the PBE results, the central feature remains. Different configurations have energies that are nearly identical. Table I also shows that the various high quality basis sets used by different electronic structure programs give slightly different answers that might change the energetic ordering.

The new low-lying structures  $\text{Si}_{16a}$ ,  $\text{Si}_{16b}$ ,  $\text{Si}_{17a}$ ,  $\text{Si}_{17b}$ ,  $\text{Si}_{18a}$  and  $\text{Si}_{19a}$  which were found with DMHM and the reference structures  $\text{Si}_{16}$  [11],  $\text{Si}_{17}$  [6],  $\text{Si}_{18}$  [6] and  $\text{Si}_{19}$  [7] were already presented in [15]. The structure  $\text{Si}_{13}$  was found by Ho *et al.* [6], the rotationally symmetric  $\text{Si}_{13d}$  structure was recently proposed by Hartke [25],  $\text{Si}_{13f}$  by Röthlisberger *et al.* [26] and  $\text{Si}_{13g}$  by Jeong *et al.* [27]. Using DMHM [15] we found new low-lying structures  $\text{Si}_{13a}$ ,  $\text{Si}_{13b}$ ,  $\text{Si}_{13c}$  and  $\text{Si}_{13e}$ . From the QMC results in Table I we conclude that the  $\text{Si}_{13d}$  and  $\text{Si}_{13a}$  configurations are the lowest energy structures. The new  $\text{Si}_{13a}$  structure found with DMHM contains the stable  $\text{Si}_6$  subunit [28].

After having discussed the limitations of computa-

TABLE I: The energy differences in mHa between the low energy geometries  $\text{Si}_{13a}$ ,  $\text{Si}_{13b}$ ,  $\text{Si}_{13c}$ ,  $\text{Si}_{13d}$ ,  $\text{Si}_{13e}$ ,  $\text{Si}_{13f}$ ,  $\text{Si}_{16a}$ ,  $\text{Si}_{16b}$ ,  $\text{Si}_{17a}$ ,  $\text{Si}_{17b}$ ,  $\text{Si}_{18a}$ ,  $\text{Si}_{19a}$  and the reference structures  $\text{Si}_{13}$ ,  $\text{Si}_{16}$ ,  $\text{Si}_{17}$ ,  $\text{Si}_{18}$  and  $\text{Si}_{19}$ , proposed earlier as global minima in DFT. The Gaussian [17] calculations used the 6-311G(2d) basis and the DMol3 2005 [18, 19] calculations the extended basis set. The CPMD [20] calculations were performed with an accurate pseudopotential [21] with a 35 Ry plane wave cutoff and a 30 Å simulation cell.

Cluster	B3LYP GAUS.	PBE DMOL	PBE CPMD	PBE GAUS.	DMC
$\text{Si}_{13}$	0.0	0.0	0.0	0.0	0.0
$\text{Si}_{13a}$	-11.7	6.3	7.1	5.3	$-3.3 \pm 1.0$
$\text{Si}_{13b}$	-1.4	9.5	13.2	11.5	$5.7 \pm 1.0$
$\text{Si}_{13c}$	8.6	4.7	3.1	3.1	$6.4 \pm 1.0$
$\text{Si}_{13d}$	-6.7	-2.9	0.9	0.6	$-5.7 \pm 1.1$
$\text{Si}_{13e}$	3.6	3.9	4.1	4.2	$6.1 \pm 1.0$
$\text{Si}_{13f}$	4.2	7.0	8.5	8.0	$10.6 \pm 1.0$
$\text{Si}_{13g}$	-6.3	-0.8	2.6	2.3	$0.0 \pm 1.1$
$\text{Si}_{16}$	0.0	0.0	0.0	0.0	0.0
$\text{Si}_{16a}$	24.0	-0.2	-6.0	-3.7	$9.9 \pm 1.4$
$\text{Si}_{16b}$	9.5	0.9	0.9	1.4	$8.3 \pm 1.4$
$\text{Si}_{17}$	0.0	0.0	0.0	0.0	0.0
$\text{Si}_{17a}$	7.4	8.4	2.6	2.7	$6.3 \pm 1.5$
$\text{Si}_{17b}$	10.2	11.6	8.4	8.4	$13.2 \pm 1.7$
$\text{Si}_{18}$	0.0	0.0	0.0	0.0	0.0
$\text{Si}_{18a}$	31.3	17.1	10.0	10.2	$23.9 \pm 1.6$
$\text{Si}_{19}$	0.0	0.0	0.0	0.0	0.0
$\text{Si}_{19a}$	15.4	-1.0	-4.2	-1.9	$2.1 \pm 1.7$

tional approaches in determining the total energy of silicon clusters with the necessary accuracy let us discuss the physical effects that can change the energetic ordering. For the  $\text{Si}_{13}$ ,  $\text{Si}_{13a}$  and  $\text{Si}_{13d}$  clusters we have zero point energies of 24.0, 25.0 and 24.5 mHa. For the  $\text{Si}_{19}$  and  $\text{Si}_{19a}$  we have 38.8 and 38.0 mHa. So the differences of the zero point energies are all of the order of mHa and thus not negligible, but do not change the energetic ordering for the clusters we studied. In order to study the entropic effects we calculated the rotational and vibrational free energy based on the harmonic frequencies obtained from density functional (PBE) calculations [29]. The translational free energy does not depend on the configuration and was therefore not considered. If one compares the sum of the rotational and vibrational free energy for non-symmetric configurations, one typically finds differences of about 0.5 mHa at room temperature and about 1 mHa close to the melting point of the clusters [30]. This might change the energetic ordering, but we did not find a case where it actually does.

The situation is different if one compares a symmetric with a non-symmetric configuration. Silicon occurs in nature mainly as  $^{28}\text{Si}$  or  $^{29}\text{Si}$  isotope. The predominant isotope for silicon  $^{28}\text{Si}$  (abundance  $\sim 92\%$  [31]) has mass 28 and no nuclear spin, the  $^{29}\text{Si}$  isotope (abundance  $\sim 5\%$  [31]) has mass 29 and nuclear spin 1/2. When studying configurations with rotational symmetry, we

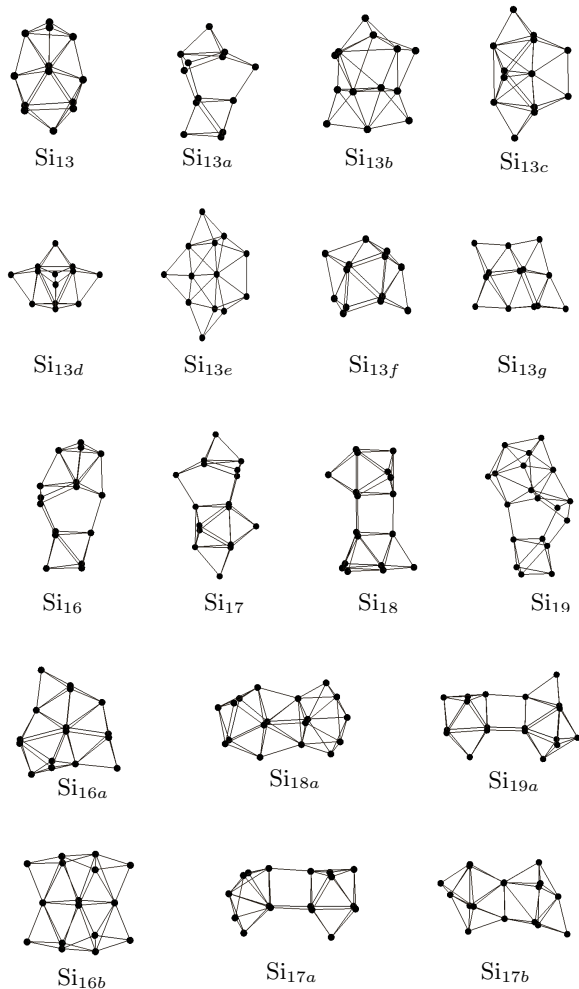


FIG. 3: Symmetrized geometries of low-lying  $\text{Si}_{13}$ ,  $\text{Si}_{16}$ ,  $\text{Si}_{17}$ ,  $\text{Si}_{18}$  and  $\text{Si}_{19}$  isomers.

will consider pure clusters consisting only of  $^{28}\text{Si}$  atoms since the presence of a  $^{29}\text{Si}$  atom would destroy the rotational symmetry. One can easily estimate from the abundancies of the isotopes that  $\sim 34\%$  of  $\text{Si}_{13}$  clusters will be pure clusters. For such a cluster with rotational symmetry, the order of the rotational subgroup enters into the formula for the rotational free energy. This leads to a weaker decrease of the free energy for symmetric configurations compared to non-symmetric configurations and thus favors non-symmetric structures. In Fig. 4 we present the free energy curves for the structures  $\text{Si}_{13a}$  and  $\text{Si}_{13d}$  as a function of temperature with the  $\text{Si}_{13}$  free energy chosen as reference energy. The width of the bands for  $\text{Si}_{13a}$  and  $\text{Si}_{13d}$  represents the statistical errors in the QMC energies with respect to that of structure  $\text{Si}_{13}$ . For the symmetric  $\text{Si}_{13a}$  configuration the order of the rotational subgroup is 3, for  $\text{Si}_{13d}$  it is 2 and for  $\text{Si}_{13}$  it is 1. This leads to a reversal of the energetic ordering of the structures  $\text{Si}_{13}$  and  $\text{Si}_{13a}$  in the interval between 250 and 650 K. Because of the entropic effect the  $\text{Si}_{13}$

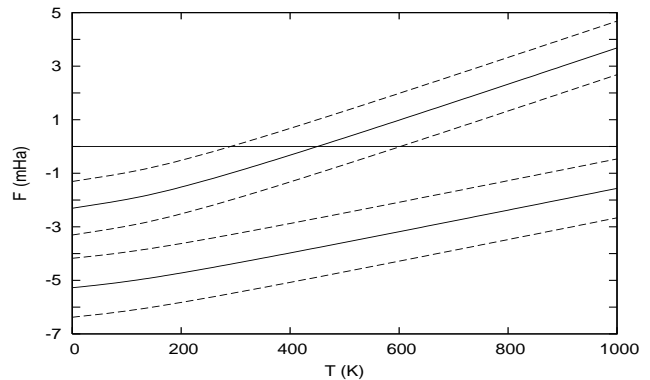


FIG. 4: The sum of the electronic (QMC, with errors), rotational and vibrational (including zero point) free energy contributions for  $\text{Si}_{13a}$  (upper band) and  $\text{Si}_{13d}$  (lower band) configurations as a function of temperature with the  $\text{Si}_{13}$  free energy chosen as reference energy (solid line, set to 0).

configuration, which is the highest at zero temperature, becomes the lowest at temperatures above 1000 K. At room temperature the  $\text{Si}_{13a}$  and  $\text{Si}_{13d}$  bands are separated by an energy gap in the range between  $\sim 1.2\text{mHa}$  and  $\sim 5.5\text{mHa}$ . This corresponds to a Boltzmann weight in the range between 0.7% and 30%.

These considerations are only valid for clusters consisting purely of  $^{28}\text{Si}$  atoms. The presence of a  $^{29}\text{Si}$  isotope destroys the rotational symmetry. One can estimate from the abundancies of the isotopes that  $\sim 24\%$  of  $\text{Si}_{13}$  clusters will contain one  $^{29}\text{Si}$  isotope. If one  $^{28}\text{Si}$  atom with nuclear spin 0 is replaced by a  $^{29}\text{Si}$  isotope which has spin 1/2, the nuclear wave-function is a doublet and additional degeneracy comes from the fact that the isotope can replace any of the atoms. For a non-symmetric cluster with  $N$  atoms the degeneracy is thus  $2N$ . For a symmetric cluster that has several equivalent atoms the degeneracy is however reduced. In the case of the  $\text{Si}_{13a}$  structure there are for instance only 5 non-equivalent sites,  $\text{Si}_{13d}$  has 6 and  $\text{Si}_{13}$  has 9. The nuclear entropy thus favors  $\text{Si}_{13}$  over  $\text{Si}_{13d}$  by  $-kT \ln(\frac{9}{6})$  which is  $\sim 0.4\text{mHa}$  at room temperature. In addition, the vibrational and rotational entropy contributions are slightly changed by the presence of an isotope leading to an effect of the same order of magnitude.

Up to now we have concentrated on the 10 lowest structures. Considering higher lying configurations, the energetic spacing between configurations decreases even further. This can be inferred from the fact the the configurational density of states, defined as the number of configurations per energy interval, increases strongly. This is shown in Fig. 5 for the  $\text{Si}_{17}$  cluster.

Several simulations have shown that the lowest energy structures for Si clusters with less than 20 atoms are non-spherical whereas larger clusters prefer to be spherical [1, 8]. In these studies the non-spherical to spheri-

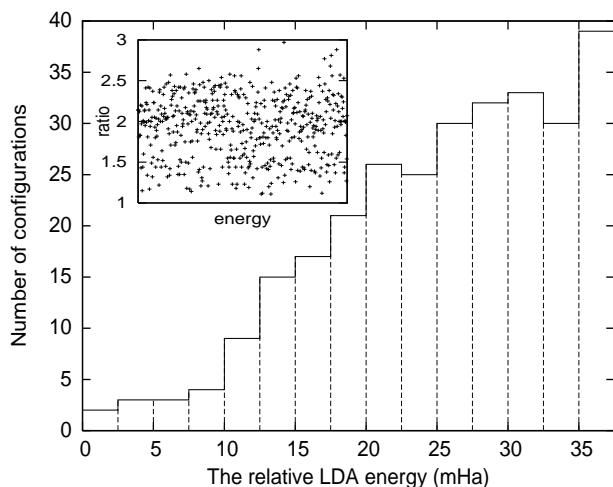


FIG. 5: The configurational density of states for  $\text{Si}_{17}$ . The inset shows the ratio of the largest and smallest eigenvalues of the moment of inertia tensor for various low-lying  $\text{Si}_{17}$  configurations.

cal transition was obtained by considering the putative ground state configurations. The inset in Fig. 5 shows the ratio between the largest and smallest eigenvalues of the moment of inertia tensor for various low-lying  $\text{Si}_{17}$  clusters. A ratio of 1 corresponds to a spherical geometry, while larger values correspond to non-spherical structures. For a given cluster size we observe in Fig. 5 that the occurrence of non-spherical and spherical structures is independent of energy.

In summary, we have shown that there exists a large number of configurations for certain silicon clusters that are energetically extremely close to the ground state. This feature was observed for  $\text{Si}_{13}$  and  $\text{Si}_{19}$  and it will presumably be even more important for larger cluster sizes that were not studied in this work. As a consequence, entropy effects that are usually neglected can change the energetic ordering of the lowest configurations. Entropy disfavors symmetric clusters  $\text{Si}_n$  in the range  $13 \leq n \leq 19$  which contain in most cases no  $^{29}\text{Si}$  isotope or one  $^{29}\text{Si}$  isotope. Larger clusters will on average contain more than one  $^{29}\text{Si}$  isotope and the symmetry related effects discussed above do not exist. However, for larger clusters the 10 lowest configurations can be expected to lie within an even smaller interval. The entropic effects not related to symmetry considerations might thus easily change the energy order of clusters with more than 19 atoms. Even if there is no reordering, different structures can be so close in free energy that a mixture of two or more configurations will be found at thermal equilibrium. As a consequence measured properties of clusters can be some average of the properties of several low-lying isomers. We thank Markus Meuwly for discussions, X. C. Zeng and A. Tekin for the  $\text{Si}_{13}$  cluster data, the Swiss National Science Foundation for financial support and the staff

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